Chemistry of Vanadium-Carbon Single and Double Bonds

Chemie van Vanadium-Koolstof Enkele en Dubbele Bindingen

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Chemistry of Vanadium-Carbon Single and Double Bonds

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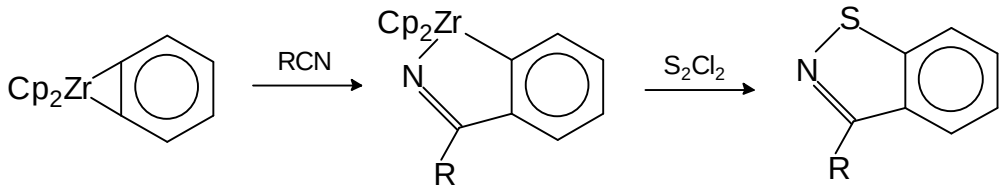
Abbreviations used in the text:

Cp	C_5H_5, cyclopentadienyl
Cp*	C_5Me_5, pentamethylcyclopentadienyl
dmpe	$Me_2PCH_2CH_2PMe_2$, 1,2-bis(dimethylphosphino)ethane
Me	CH_3, methyl
Et	C_2H_5, ethyl
Pr	C_3H_7, propyl
Bu	C_4H_9, butyl
Ph	C_6H_5, phenyl
Mes	2,4,6-$C_6H_2Me_3$, mesityl
TMS	Me_4Si, tetramethylsilane
THF	C_4H_8O, tetrahydrofuran
NMR	Nuclear Magnetic Resonance
IR	Infrared
ROMP	Ring-Opening Metathesis Polymerization

General Introduction

Metal-carbon single and double bonds. Transition metal-carbon σ-bonds play a key role in many industrially important homogeneous catalytic processes such as hydroformylation, polymerization of α-olefins and carbonylation of methanol,[1] and are also becoming increasingly more important in selective formation of organic products by stoichiometric reactions. An example of the last is the synthesis of main group heterocyclic compounds, which have long played a dominant role in medicinal chemistry and in the science of crop protection,[2] by transfer of the carbon fragment from zirconacycles to main group halides (eq 1).[3]



(1)

At the heart of the reactivity of transition metal-carbon σ-bonds lies the C,C-couplings reaction which arises from insertion of carbon containing unsaturated substrates in the metal-carbon bond and provides an excellent tool for the build up of C-C skeletons. In combination with other transition-metal catalyzed processes such as C-H activation,[4] C,C-coupling will become even more important for the chemical industry in the future, when feedstocks will change from oil to natural gas and environmental demands will limit the use of more traditional, salt producing means of carbon-carbon bond formation.

Well-defined complexes containing formal metal-carbon double bonds (metallaolefins) can be divided into two classes. First discovered in 1964,[5] Fisher-type metallaolefins or metal carbenes, which possess low-oxidation state metal centers and electrophilic carbene carbon atoms with hetero-atom substituents, form the largest class (Fig. 1, left). A smaller, but fast growing class is formed by the Schrock-type metallaolefins or metal alkylidenes, discovered in 1974,[6] which have metal centers generally in their highest oxidation state and nucleophilic carbene carbon atoms with hydrocarbyl substituents (Fig. 1, right).

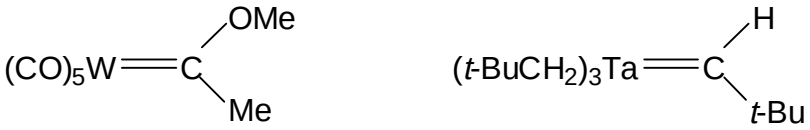
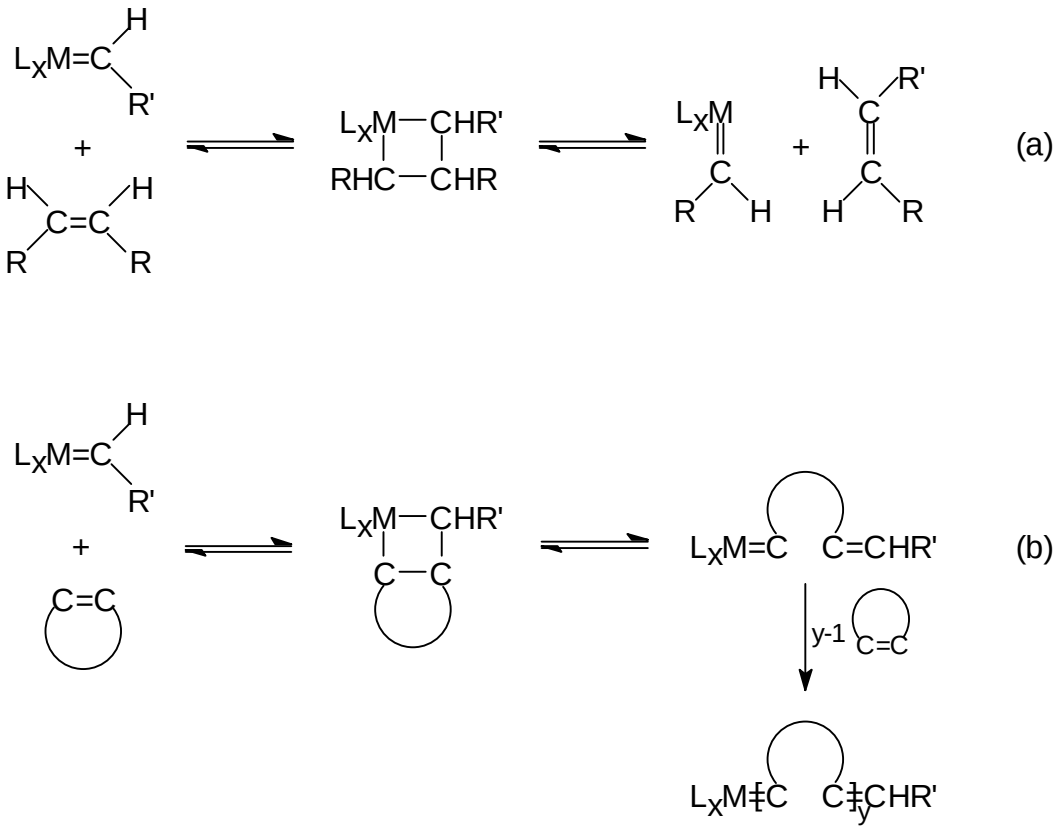


Figure 1. First examples of Fischer and Schrock-type metallaolefins.

The two classes also differ strongly in the way in which the carbene ligand is generated: metal carbenes can be prepared *via* a nucleophilic attack on a metal-bonded

carbonyl ligand, whereas metal alkylidenes are generally formed *via* an α-hydrogen abstraction in high-valent metal alkyl complexes, though other, less used, methods are known.[7]

Especially the metal alkylidenes find application as intermediates in olefin metathesis reactions,[8] a reaction in which an interchange takes place of carbon atoms between pairs of double bonds. In the now generally accepted "carbene-mechanism' for olefin metathesis, first proposed in 1970 by Herisson and Chauvin,[9] a metal alkylidene forms a metallacyclobutane with an olefin. Decomposition of this metallacyclobutane in a productive metathesis step gives a new olefin and a new alkylidene, which can react again with an olefin (Scheme 1a). When both carbon atoms are linked, as in cyclic olefins or alkynes, the new olefin and alkylidene remain in one molecule, and the addition of more olefin will lead to polymer formation, (Scheme 1b). These polymers, produced by so-called ring-opening metathesis polymerization (ROMP), find applications in for instance automobile bumpers, due to their rubber-like properties.



Scheme 1. The generally accepted 'carbene-mechanism' of olefin metathesis reactions.

Although one of the first reported examples of ROMP of norbornene used a catalyst system based on the 3d metal Ti,[10] the 4/5 d metals Mo, W and Re are used in almost all commercial metathesis processes and also constitute the main class of discrete metal

alkylidenes that are efficient catalysts for olefin metathesis. A review covering the alkylidene chemistry of the early-transition metals through 1991 appeared recently.[11]

Organovanadium chemistry. Since the discovery of Cp_2V 40 years ago[12] the development of organanovanadium chemistry has, with a few exceptions, been relatively slow,[13] especially in comparison with neighboring organotitanium chemistry. Disregarding vanadium carbonyls, the first well-characterized examples of vanadium complexes containing σ-bonded carbon ligands were $V(CH_2SiMe_3)_4$ and $O=V(CH_2SiMe_3)_3$, reported by Wilkinson *et al.* in 1972.[14] The first nucleophilic alkylidene complex of vanadium, CpV(CH-*t*-Bu)dmpe, was reported as late as 1989 by Hessen and Teuben.[15] The unusually high incidence of paramagnetism and the low stability of the higher valent hydrocarbyl complexes form the main causes for the slow development of organovanadium chemistry.

Nevertheless, during the last decade the number of studies of the hydrocarbyl chemistry of mid and high-valent vanadium has increased severely, mainly due to the work of a small number of groups. Both Preuss *et al.*[16] and Maatta *et al.*[17] have reported the syntheses of homologous series of imido alkyl complexes of d^0 vanadium (Fig. 2, A and B). Horton *et al.* published the first structurally characterized alkylvanadium(V) complex, $Li[(RN)_2VMe_2]$ (R = *t*-Bu_3Si) (Fig. 2, C),[18] and reported on the thermal decomposition of the bis(amido) imido methylvanadium(V) complexes $RN=V(NHR)_2Me$ and C-H activation of a range of substrates, including methane, by the bis(imido) amido decomposition product $(RN=)_2V(NHR)$.[19] Recently, an extensive study on the insertion and oxidation chemistry of $VMes_3$ was published by Floriani *et al.*.[20] Based on $CpVCl_2(PMe_3)_2$,[21] Teuben *et al.* developed a range of V(III) hydrocarbyl complexes[15,22] and studied their thermal decomposition, which culminated in the synthesis of a vanadium(III) alkylidene (Fig. 2, D).[15]

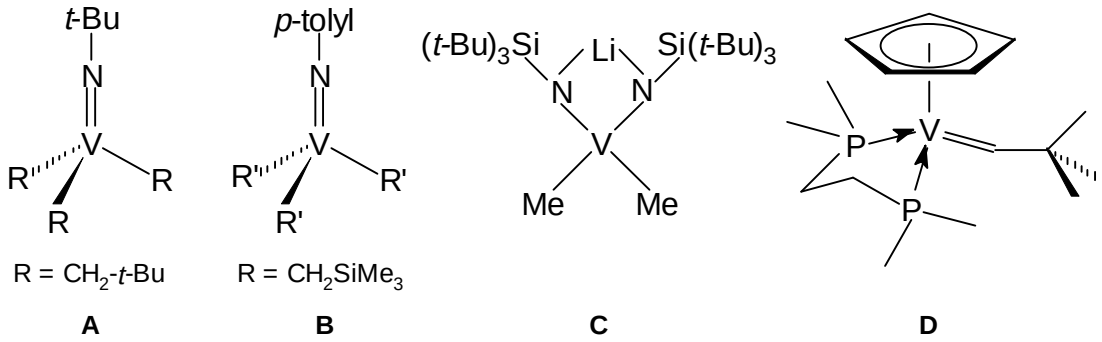


Figure 2. Some recent examples of hydrocarbyl complexes of mid and high-valent vanadium.

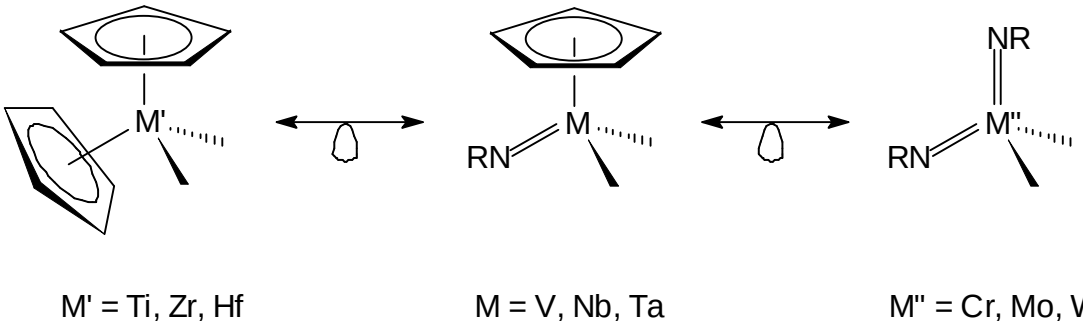
Ligand systems. Pentahapto cyclopentadienyl (η^5-Cp) and pentamethylcyclopentadienyl (η^5-Cp*) have found wide use as ancillary ligands in transition metal chemistry.[23] Especially for the early transition metals (groups 3-5) the study of metallocene (Cp_2M) derivatives has led to

increased understanding of fundamental processes in organometallic chemistry. The Cp_2M-fragment has only a limited set of orbitals available for the bonding of other ligands and substrates, which allows rationalisation of many reactions observed by simple MO-theory,[24] but limits the reactivity potential of the metal ion. The development of mono(cyclopentadienyl) systems has further enlarged the scope of reactivity of the early-transition metals.

For vanadium the development of hydrocarbyl chemistry of the higher oxidation states (IV and V) based on cyclopentadienyl ligands has been slow, due to the absence of suitable precursors and the low stability of hydrocarbyl complexes derived from Cp_2VCl_2.[25] The use of oxo and especially imido ligands permitted the development of a more systematic hydrocarbyl chemistry of high-valent vanadium.[16-19] Oxo and imido ligands are particularly suited to the stabilization of high-oxidation-state transition metal complexes due to their ability to participate in extensive ligand-to-metal π-donation.[26] The imido ligand has the additional advantage that it contains an organic substituent through which the steric and electronic properties of the complex may be influenced, for instance to prevent imido-bridge formation.

Cyclopentadienyl and imido ligands both interact with a metal *via* 1σ and 2π donor interactions and therefore possess frontier orbitals with similar symmetry properties. Combination of a cyclopentadienyl ligand and an imido ligand on a group 5 metal M results in half-sandwich imido fragments CpM(NR), which are thought to have frontier orbitals with symmetry properties similar to those of group 4 metallocene fragments Cp_2M'. This so-called isolobal relationship[24a,27] (Scheme 2) can also be extended to non-cyclopentadienyl bis(imido) complexes of the group 6 metals.

Quantum-chemical calculations have confirmed the isolobal relationships for the fragments shown in Scheme 2.[28] Although the isolobal analogy is, strictly speaking, a structural analogy, ligand substitution studies indicate that close similarities in reactivity exist for these fragments as well.[28,29]



Scheme 2. Isolobal relationships in early-transition metal cyclopentadienyl-imido systems.

In view of these observations, introduction of the half-sandwich imido ligand system in vanadium chemistry could give rise to increased stability of vanadium-carbon bonds, thus allowing isolation and reactivity studies of d^0 vanadium hydrocarbyl complexes containing single and double vanadium-carbon bonds.

Characterization of organo-vanadium complexes. The use of NMR spectroscopy, which has become the major technique for structure assignment and reactivity study in organometallic chemistry, is severely limited in organovanadium complexes by the frequently occurring paramagnetism. The ^{1}H NMR resonances in these compounds are usually very broad ($\Delta\nu_{1/2}$ of 300-700 Hz), and all coupling information is lost. Furthermore, the chemical shifts can vary over a large range ($\pm$ 1200 ppm), and are very unpredictable. Relaxation phenomena may cause resonances to be unobservable.[30]

Paramagnetism can however sometimes be avoided by variation of the ligand set. Tetrahedral d^2 complexes tend to form high-spin complexes, but incorporation of ligands capable of forming double bonds to vanadium, like carbene or imido, produces diamagnetic tetrahedral complexes, presumably due to a decrease of the barrier for spin-pairing.[15] Moreover, in some cases two electron oxidation reactions, for instance oxygen transfer from epoxides to the metal center, can transform paramagnetic d^2 complexes in diamagnetic derivatives.[20a,e,31]

In the case of diamagnetic organovanadium complexes, the use of NMR spectroscopy is still somewhat limited as resonances of the nuclei directly bound to vanadium are usually strongly broadened due to unresolved coupling with the quadrupolar ^{51}V nucleus (I =7/2, natural abundance 99.76%), but this is partially compensated by the facile observation of the ^{51}V nucleus itself. Although line widths are variable and dependent on the symmetry of the vanadium complex,[15] they often allow evaluation of J_{VP} and sometimes J_{VN} coupling constants. The large shift range for ^{51}V NMR (-2200 to 1500 ppm) can cause problems with the observation of ^{51}V NMR resonances on a routine basis. Within the series of vanadium(V) oxo and imido complexes for which ^{51}V NMR shifts were determined a number of consistent shift-structure relations are evident.[17,32]

Other means of characterization like functional group identification by IR spectroscopy and elemental analysis are merely used to determine the stoichiometry of the compounds, while single crystal X-ray diffraction is often indispensable for the determination of coordination geometries and more detailed structural information, especially for the more complicated (paramagnetic) molecules.

Goal and survey of this investigation. The goal of this research was to extend the hydrocarbyl chemistry of mid and high-valent vanadium, with special emphasis on the

development of synthetic routes to vanadium alkylidenes and on reactivity of vanadium-carbon single and double bonds towards small, unsaturated organic molecules.

Chapter 1 describes some aspects of hydrocarbyl complexes in the mono(cyclopentadienyl) vanadium(III) system. The syntheses of alkynyl complexes and a vanadium(I) benzyne complex, which can alternatively be viewed as vanadium(III)-benzometallacyclopropene, are reported, as well as reactivity studies of this last compound and of mono(cyclopentadienyl) vanadium(III) alkylidenes. In chapter 2 the cyclopentadienyl ligand is temporarily not used. The attempted syntheses of homoleptic alkyl complexes of vanadium(III) is described, along with the reactivity of the mid and high-valent vanadium alkyl complexes that were obtained. Evidence for ROMP of norbornene by d^0 vanadium alkylidenes formed *in situ* is presented. In chapter 3-5 the attention is focused on the half-sandwich imido ligand system. In chapter 3 the synthesis of a half-sandwich vanadium(V) dichloride containing a bulky arylimido ligand and the reactivity of half-sandwich arylimido dichlorides towards alkylating reagents is described. It is noted that the stability of high-valent vanadium-carbon bonds is not improved significantly by the applied ligand system. Therefore, in chapter 4 the attention is turned to half-sandwich imido vanadium(III) complexes stabilized by phosphine ligands, which can be obtained straightforwardly by magnesium reduction of the corresponding dichlorides. One of the phosphine ligands can be replaced under mild conditions by a range of π-acceptor ligands and one and two-electron oxidants. In chapter 5 this behavior is used to synthesize the first d^0 vanadium alkylidenes through introduction of alkylidene moieties, obtained from phosphoranes or ring-opening of 3,3-disubstituted cyclopropenes, on reduced half-sandwich imido vanadium complexes. The reactivity of these alkylidenes in olefin metathesis like reactions is discussed and compared with the reactivity of the corresponding half-sandwich imido niobium alkylidenes, which can in some cases be obtained by the same methodology.

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